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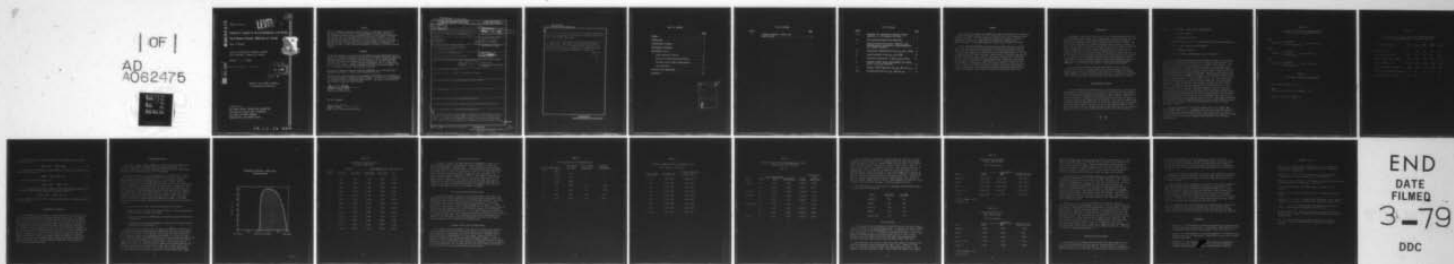
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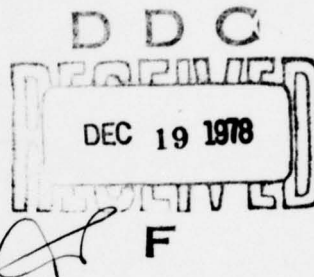
FEASIBILITY STUDIES OF AN ELECTROCHEMICAL TEST METHOD  
FOR NITROGEN TETROXIDE COMPATIBILITY TESTING

TASK II REPORT

UNITED TECHNOLOGIES RESEARCH CENTER  
EAST HARTFORD, CONNECTICUT 06108

AUTHOR: C. T. BROWN

NOVEMBER 1978



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Prepared for  
AIR FORCE ROCKET PROPULSION LABORATORY  
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AIR FORCE SYSTEMS COMMAND  
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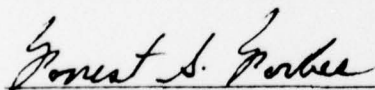
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## FOREWORD

The work described in this report was performed at United Technologies Research Center, East Hartford, Connecticut for the Air Force Rocket Propulsion Laboratory under Contract F04611-77-C-0020, initiated March 1, 1977 and ending November 30, 1978. Those who participated in the performance of the work under this contract were: Dr. C. T. Brown, Principal Investigator, Mr. L. J. Spadaccini, Dr. H. T. Couch, Chief, Chemical Technologies Section and Program Manager: Ms. P. D. DeFelice, Mr. Scott T. Kehoe and Mr. Gene Lind.

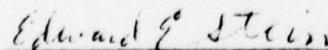
The work was conducted under the technical management of Lt. William Leyden, USAF/LKCP and Forrest S. Forbes, Chief Propellant Section.

This report has been reviewed by the Information Office/XOJ and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations. This report is unclassified and suitable for general public release.



FORREST S. FORBES, Chief  
Propellant Systems Section

FOR THE COMMANDER



EDWARD E. STEIN  
Deputy Chief, Liquid Rocket Division

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of ten to eleven value percent in order to obtain compatibility data. This concentration corresponds to the high density acid phase of the  $\text{N}_2\text{O}_4$  -  $\text{H}_2\text{O}$  system.

Above one to two value percent water a small portion of the high density acid phase is formed which can produce localized corrosion. It is suggested that corrosion in the high acid phase should be considered for further study even though the overall water concentration is quite low.

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## SUMMARY

The UTRC Electrochemical Test Method was used to investigate the compatibility of AA6061-T6, 304LSS, Ti6Al4V, Inconel X750 and Pt-10% Ir with propellant grade nitrogen tetroxide. This test method was applied successfully in previous measurements of material compatibility with hydrazine (AFRPL Contract F04611-74-C-0041) and monomethylhydrazine (AFRPL Contract F04611-77-C-0020).

It has been determined that electrochemical methods can only be applied using cell configurations having internal resistances considerably below  $10^5$  ohms. With the present cell configuration (1 cm<sup>2</sup> electrode surface area and 3 mm electrode spacing), the resistivity drops from approximately  $5 \times 10^5$  ohms to approximately  $10^2$  ohms as the water concentration is increased from approximately ten to eleven volume percent. This water concentration corresponds to the high-density acid phase of the N<sub>2</sub>O<sub>4</sub>-H<sub>2</sub>O system. Above one to two volume percent water concentration, a small portion of the high-acid phase (44 mole percent HNO<sub>3</sub>) is formed which, due to its higher chemical activity and low surface tension, can produce localized corrosion in crevices around swage fittings or valve seats. This corrosion in the high-acid phase should be considered even though the overall water concentration level may be quite low.

## INTRODUCTION

Experimental studies have been carried out to evaluate the applicability of an electrochemical test method for the measurement of compatibility of selected metals with nitrogen tetroxide ( $N_2O_4$ ) (Military Specification P-26539C-2). This work was performed under Task II of AFRPL Contract F04611-77-C-0020. The test method, developed at the United Technologies Research Center, provides a measure of the natural propellant decomposition rate on the surface of the metal under investigation. The time base is then altered by electrolysis of the system at some multiple of the natural decomposition rate. As a result, a simulated time scale is achieved in which the propellant decomposition rate can be predicted up to fifteen years while the actual time required for the tests is on the order of one to two months, depending on the particular metal tested. This method has been successfully applied in previous measurements of material compatibility in propellant grade hydrazine ( $N_2H_4$ ) and monomethylhydrazine (MMH) (Ref. 1 and 2) as well as in Task I of the present investigation.

In this report, available real-time compatibility data for  $N_2O_4$  are reviewed and the results of  $N_2O_4$  compatibility testing, using the electrochemical test method, are discussed. Test results are presented for Ti6Al4V, 304LSS, AA6061-T6, Inconel X750 and Pt-10% Ir alloys. In addition, the decomposition mechanism for  $N_2O_4$  and the  $N_2O_4$ - $H_2O$  phase diagram are also discussed.

## ELECTROCHEMICAL THEORY

The electrochemical test method used in this investigation is based on the measurement of current flow at or very near the equilibrium potential between a metal surface and a liquid phase (electrolyte). This current is proportional to the rate of electron transfer across the metal/liquid interface. The rate of electron transfer is converted to the rate of reaction of a specific species on the metal surface using a known reaction mechanism. This method is known as the resistance polarization method (Ref. 3), since the current-voltage relationship obeys Ohm's law at potentials very close to the equilibrium potential of the metal-electrolyte couple. The natural current flow (reaction rate) at the equilibrium potential is  $i_o$ , the exchange current density, which can be expressed as:

$$i_o = \frac{RT}{F} \cdot \frac{di}{d\eta}$$

where:  $i_o$  = exchange current density (amperes/cm<sup>2</sup>)

$i$  = current (amperes)

$\eta$  = overpotential (volts)

$di/d\eta$  = the slope of the  $i$ - $\eta$  relationship at the equilibrium potential

$R$  = the gas constant (Joules/°K/mole)

$T$  = temperature (deg K)

$F$  = the Faraday (96,488 amp-sec g mole equivalent)

Once  $i_o$  has been established for a given time of exposure, the time-base of the test is extended by electrolysis of the system at some multiple of  $i_o$ . The ratio of the electrolysis current to the exchange current density is the simulation factor for the time increment of interest. The exchange current densities are used to calculate the rate and amount of decomposition based on the mechanism for the reaction of  $N_2O_4$  on a metal surface. Equations for calculating the decomposition rates of  $N_2H_4$ , MMH, and  $N_2O_4$  from exchange current density measurements are summarized in Table I. The comparison provides a perspective for the relative extent of decomposition of the three liquids studied under the existing contract. Also included in Table I are the most probable decomposition mechanisms for each of the three compounds. The decomposition mechanisms for  $N_2H_4$  and MMH have been documented in previous reports (Refs. 1 and 4). The mechanism for  $N_2O_4$  decomposition was derived from the literature, and it should be noted that the electrochemical reaction is written in terms of water as a co-reactant. Therefore, possible reactions in  $N_2O_4$  must be considered in terms of its solvent properties. In some cases certain nitrosyl compounds yield nitrosylium (NO<sup>+</sup>) ions in the solvent; however, the low conductivity ( $2 \times 10^{-13}$  ohm<sup>-1</sup> cm<sup>-1</sup>) and the lack of decomposition by electrolysis preclude any extensive auto-ionization process (Ref. 6). Pure  $N_2O_4$  is non-polar, and dissociation into ions apparently occurs only when highly polarizing groups are added to the solvent. One such polarizing group is water, a natural contaminant in  $N_2O_4$ .

The physical properties of  $N_2O_4$  are compared with those of  $N_2H_4$ , MMH,  $H_2O$  and UDMH in Table II. It is apparent that  $N_2O_4$  has a high vapor pressure, a low boiling point and, most particularly, a very low dielectric constant. It is this latter factor which controls the ionizing properties of  $N_2O_4$  as a solvent and places restrictions on electrochemical measurements at very low water concentrations.

TABLE I-A

Constants for Conversion of Exchange Current  
Densities ( $i_o$ ) to Decomposition Rates



$$\text{mg/cm}^2/\text{yr} = \frac{i_o \text{ (amps/cm}^2\text{)}}{1.21 \times 10^1 \text{ amp-sec/mg}} \times 3.154 \times 10^7 \text{ sec/yr}$$



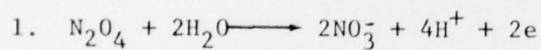
$$\text{mg/cm}^2/\text{yr} = \frac{i_o \text{ (amps/cm}^2\text{)}}{4.190 \text{ amp-sec/mg}} \times 3.154 \times 10^7 \text{ sec/yr}$$



$$\text{mg/cm}^2/\text{yr} = \frac{i_o \text{ (amp/cm}^2\text{)}}{2.098 \text{ amp-sec/mg}} \times 3.154 \times 10^7 \text{ sec/yr}$$

TABLE I-B

Most Probable Decomposition Mechanisms



(MMH)

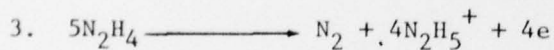
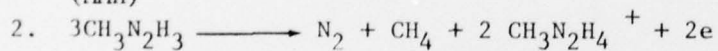


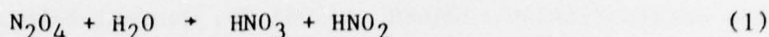


TABLE II

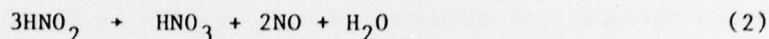
Physical Properties of Water, Hydrazine, Monomethylhydrazine,  
Unsymmetrical Dimethylhydrazine, and Nitrogen Tetroxide

<u>Physical Property</u>	<u>H<sub>2</sub>O</u>	<u>N<sub>2</sub>H<sub>4</sub></u>	<u>MMH</u>	<u>UDMH</u>	<u>N<sub>2</sub>O<sub>4</sub></u>
Melting Point (°C)	0	1.53	-52	-57	-11.2
Normal Boiling Point (°C)	100	114	88	62	21.1
Vapor Pressure (298°K) (mmHg)	23.7	14.2	49	167	899
Density (298°K) (g/cc)	0.997	1.004	0.87	0.79	1.434
Viscosity (298°K) (centipoise)	0.894	0.913	0.775	0.492	0.369
Surface Tension (298°K) (dynes/cm)	72	66	34	24	25
Dielectric Constant (298°K)	80	52	19	-	2.4

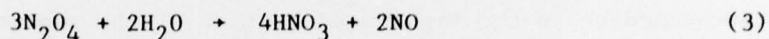
The reaction of water with  $N_2O_4$  results in the formation of nitric and nitrous acids; i.e.,



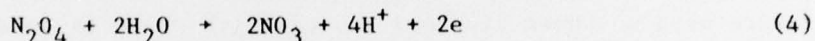
This reaction is followed by the decomposition of the nitrous acid to nitric acid and nitric oxide; i.e.,



Therefore, the overall reaction is:



If it is assumed that NO has no effect on the electrochemical properties of the system, the most probable reaction on the metal surface is;



i.e., the formation of nitric acid in which two Faradays are required per mole of  $N_2O_4$  decomposed.

#### EXPERIMENTAL TECHNIQUES

The experiments were performed in electrochemical cells using glass reference electrodes and metal test specimens imbedded in FEP Teflon. The general principles and details of the cell design are the same as previously reported (Refs. 1 and 2); however, in the present tests the electrodes were mounted in a horizontal position so that the distance between electrodes could be adjusted to compensate for the high internal resistance. The propellant grade  $N_2O_4$  was introduced directly into the cell after the entire system was flushed with dry nitrogen. All tests were conducted at 50 F (10 C) in order to minimize the pressure in the cell. In general, it was found that a very small electrode spacing (~3 mm) was necessary in order to prevent instrument overload and obtain useful results, even in cases where appreciable amounts of water were added to the system. Predetermined amounts of water were added by means of a calibrated micro syringe. The cell was then flushed with dry nitrogen and filled with propellant grade  $N_2O_4$ .

## EXPERIMENTAL RESULTS

The metals Ti6Al4V, 304LSS, AA6061-T6, Inconel X750 and Pt-10% Ir were evaluated in propellant grade  $N_2O_4$  and in  $N_2O_4$  with water added. In addition, conductivity tests were performed to define the water concentration range where electrochemical tests could be performed.

Since the addition of water to  $N_2O_4$  results in the formation of nitric acid (Reaction 3), it is necessary to evaluate the results in terms of the  $HNO_3$ - $N_2O_4$  phase diagram illustrated in Fig. 1. If the amount of water added to the system reduces the  $N_2O_4$  concentration to a value less than that corresponding to the right-hand portion of the two-phase region (indicated by the shaded area), a second phase will be formed having a composition corresponding to the left-hand portion of the two-phase region. Although the relative proportions of the two phases change as overall composition is changed, the composition of each phase remains constant. Thus, at 50 F (the operating temperature used in these studies) an acid-rich phase is formed which has a composition of 44 mole percent  $N_2O_4$  and 56 mole percent  $HNO_3$ . This composition is relatively constant over a wide temperature range, as evidenced by the almost vertical phase separation line on the acid-rich side of the phase diagram.

In view of the above, three types of experiments were performed:

- 1) Phase separation studies using capillary tubes into which predetermined amounts of water and  $N_2O_4$  were added,
- 2) Electrical conductivity measurements to determine regions of high ionic concentration,
- 3) Exchange current density measurements to determine the natural reaction rate of  $N_2O_4$  on metal surfaces.

This approach was necessary since the degree of completion of Reaction (3) is not known. Available free energy data suggest that the equilibrium constant for Reaction (3) is  $6.13 \times 10^{-6}$ ; however, this theoretical value assumes that NO is completely soluble in the  $N_2O_4$ - $HNO_3$  liquid phase. If NO is lost from the system, it can then be assumed that Reaction (3) goes to completion and the NO is lost from the liquid phase. It is then possible to calculate the equilibrium composition in terms of the amount of water added. These calculations are summarized in Table III. When this data is compared to the phase diagram (Fig. 1), two-phase separation occurs at about 1.27 volume percent water added at 50 F, i.e.,  $N_2O_4$  mole fraction of 0.915. At the same time, a single-phase region is observed below a mole fraction of 0.435 or 8.5 volume percent water added.

FIG. 1

# NITROGEN TETROXIDE – NITRIC ACID PHASE DIAGRAM

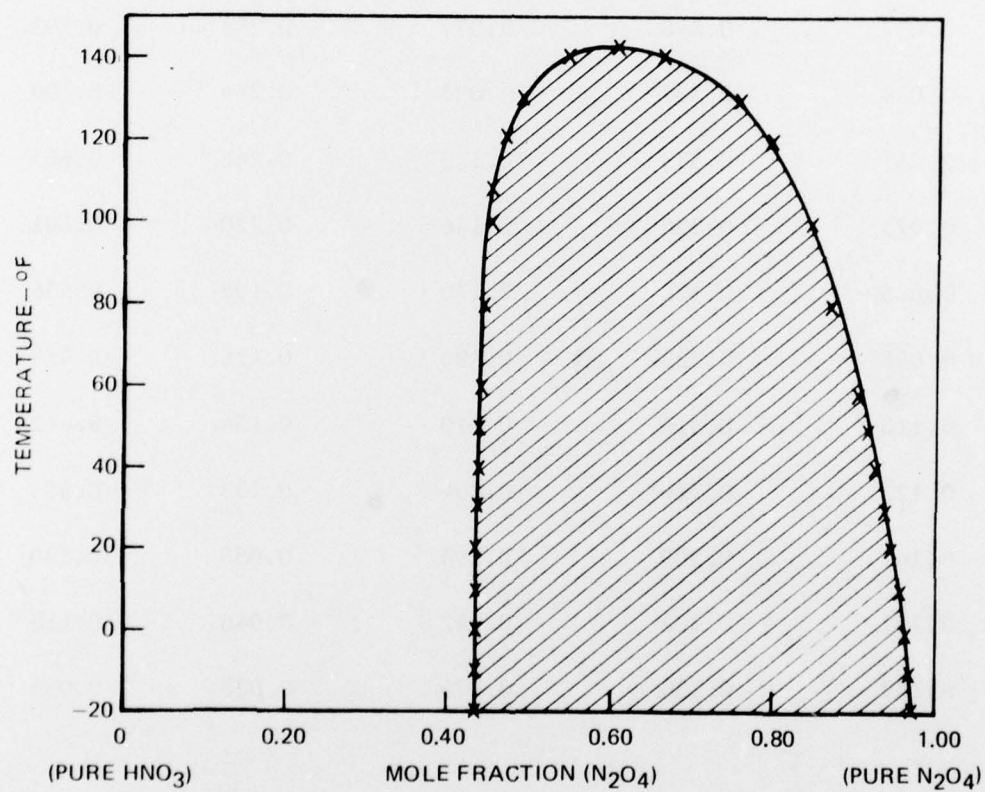




TABLE III

Equilibrium Concentrations for  
the  $\text{N}_2\text{O}_4$  -  $\text{HNO}_3$  System

Vol % $\text{H}_2\text{O}$ Added <sup>2</sup>	<u>Initial</u>		<u>Final (Equilibrium)</u>		<u>Mole Fraction</u>
	Moles $\text{H}_2\text{O}$	Moles $\text{N}_2\text{O}_4$	Moles $\text{HNO}_3$	Moles $\text{N}_2\text{O}_4$	$\text{N}_2\text{O}_4$
1	0.012	0.347	0.024	0.339	0.934
2	0.024	0.344	0.048	0.308	0.865
3	0.037	0.340	0.074	0.284	0.793
4	0.049	0.337	0.098	0.264	0.729
5	0.061	0.333	0.122	0.242	0.665
6	0.073	0.330	0.146	0.220	0.601
7	0.085	0.326	0.170	0.198	0.538
8	0.098	0.323	0.196	0.176	0.473
9	0.110	0.319	0.220	0.154	0.412
10	0.122	0.316	0.244	0.133	0.353
12	0.147	0.309	0.294	0.088	0.230
14	0.171	0.302	0.342	0.046	0.118
15	0.183	0.300	0.376	0.026	0.065

### Phase Separation Studies

In order to elucidate the phase separation phenomenon, a series of tests were performed in which varying amounts of water and  $N_2O_4$  were mixed and sealed in 3 mm diameter capillary tubes. Phase separation was not observed until approximately 1.73 weight percent (2.0 volume percent) water was added to the system. This is close to the predicted value of 1.27 volume percent  $H_2O$  which was based on complete reaction of  $N_2O_4$  with water available. The phase separation data is summarized in Table IV. The highest volume percent water level tested was 9.1 percent and, at this point, there were still two phases present. Apparently, the reaction of water with  $N_2O_4$  does not go to completion. However, the equilibrium constant must be much larger than the predicted value and the equilibrium values for the reactants and products are largely on the product side (i.e., the formation of  $HNO_3$ ).

### Electrical Conductivity Measurements

In order to determine the point at which the minimum required electrical conductivity level could be achieved in the  $N_2O_4$ - $H_2O$  system, measurements were made using a small volume conductivity cell and platinum electrodes. Tests were conducted at several levels of water addition in the range 1 to 14 percent (by volume). The results of these tests are summarized in Table V. A rapid increase in conductivity is noted at approximately 10 to 11 percent water addition. This discontinuity probably occurs at the high-acid boundary of the two-phase region of the  $N_2O_4$ - $H_2O$  system (see Fig. 1). The lack of sufficient conductivity in the low-acid phase (up to 2.0 volume percent water) precluded the use of existing electrochemical techniques. Thus, exchange current density measurements were limited to the high-conductivity phase (approximately 44 mole percent  $N_2O_4$ ) which corresponds to the formation of high-density acid.

### Exchange Current Density Measurements

The exchange current measurements confirmed the low conductivity problems in the low water concentration and two-phase regions of the  $N_2O_4$ - $H_2O$  system. The minimum current measurement level of the potentiostatic equipment used in these experiments is approximately  $10^{-3}$  micro amps. Below this level, the amplifiers automatically overload to preserve instrument integrity. Thus, as reported in Table VI, exchange current densities could be measured only at water concentration levels above 10.0 volume percent, for AA6061-T6, and 12.0 volume percent, for Inconel X750. For all other metals tested, 15.0 volume percent water was necessary before current-voltage data could be obtained.

TABLE IV

Phase Separation in the  $\text{N}_2\text{O}_4\text{-H}_2\text{O}$  System

Added $\text{H}_2\text{O}$ Concentration		Total Column Ht. (cm)	Ht. of Second Phase (cm)	Percent Second Phase
Vol%	Wt%			
0.2	0.106	22.3	-	-
0.5	0.419	17.0	-	-
1.2	0.686	19.9	-	-
2.0	1.73	14.8	0.1	0.68
4.5	3.12	19.0	1.2	6.31
8.4	6.05	19.7	2.3	12.1
9.1	6.54	19.9	2.9	14.6

TABLE V

Electrical Conductivity in the  $\text{N}_2\text{O}_4\text{-H}_2\text{O}$  System(cell constant =  $0.792 \text{ cm}^{-1}$ )

<u>Vol% <math>\text{H}_2\text{O}</math> Added</u>	<u>Resistance (<math>\Omega</math>)</u>	<u>Specific Conductivity (<math>\text{ohm}^{-1} \text{ cm}^{-1}</math>)</u>
1.0	$4.20 \times 10^5$	$1.88 \times 10^{-6}$
2.0	$3.50 \times 10^5$	$2.26 \times 10^{-6}$
3.0	$4.22 \times 10^5$	$1.86 \times 10^{-6}$
5.0	$4.16 \times 10^5$	$1.90 \times 10^{-6}$
10.0	$5.03 \times 10^5$	$1.57 \times 10^{-6}$
11.0	$1.33 \times 10^2$	$5.95 \times 10^{-3}$
12.0	$7.37 \times 10^1$	$1.07 \times 10^{-2}$
13.0	$1.42 \times 10^1$	$5.57 \times 10^{-2}$
14.0	$1.75 \times 10^1$	$4.52 \times 10^{-2}$



TABLE VI

Exchange Current Density Measurements for Several  
Metals in  $\text{N}_2\text{O}_4$ - $\text{H}_2\text{O}$  Solutions

(50 F)

Metal	Water Concentration			$i_0$ ( $\mu\text{a}/\text{cm}^2$ )	Decomposition rate ( $\text{mg}/\text{cm}^2/\text{yr}$ )
	Vol %	Wt %	Mole Fraction		
Ti6Al4V	14	9.99	0.362	$1.98 \times 10^{-1}$	2.968
	15	10.74	0.379	$6.70 \times 10^{-1}$	10.04
Pt-10% Ir	14	9.99	0.362	$3.31 \times 10^{-1}$	4.960
AA6061-T6	10	7.57	0.278	$1.44 \times 10^{-1}$	2.158
	15	10.74	0.379	$1.50 \times 10^{-1}$	2.248
Inconel X750	12	8.50	0.320	$\sim 10^{-3}$	0.015
	14	9.99	0.362	$1.05 \times 10^{-2}$	0.157
	15	10.74	0.379	$6.10 \times 10^{-2}$	0.914
304L SS	15	10.74	0.379	$5.64 \times 10^{-2}$	0.845

When the exchange current density measurements are translated into  $N_2O_4$  decomposition rates (Table VI), it is apparent that the metals that promote higher decomposition rates are Ti6Al4V, AA6061-T6 and Pt-10% Ir, while 304LSS and, especially, Inconel X750 yield lower rates. These results, with the exception of Pt-10% Ir, are opposite in order to those obtained previously for  $N_2H_4$  and MMH. Also, the absolute decomposition rates were highest in the  $N_2H_4$ - $H_2O$  system. Short-term exposure or real-time decomposition rate data for each of the three propellant systems of interest are summarized in Tables VII and VIII. The short-term decomposition rates measured for  $N_2O_4$  - 15%  $H_2O$  and  $N_2H_4$  are similar in magnitude for Inconel X750 and 304LSS. The opposite is true for Ti6Al4V, AA6061-T6 and Pt-10% Ir. MMH decomposition rates are, in all instances, much lower than the  $N_2O_4$  - 15%  $H_2O$  decomposition rates.

Using the  $N_2H_4$  data as a base line, the  $N_2O_4/N_2H_4$  and  $N_2O_4/MMH$  decomposition rate ratios are as follows:

<u>Metal</u>	<u><math>N_2O_4/N_2H_4</math></u>	<u><math>N_2O_4/MMH</math></u>
AA6061-T6	281	44.0
Ti6Al4V	182	108
Pt-10% Ir	9.42	12.2
304LSS	1.57	3.53
Inconel X750	1.25	3.13

#### Data Comparison

It was possible to obtain short-term compatibility data for several metals in the acid region of the  $N_2O_4$ - $H_2O$ - $HNO_3$  system. It appears that metals normally used with hydrazine and monomethylhydrazine are not satisfactory for use with  $N_2O_4$ , particularly if the system becomes contaminated with water. Surprisingly, Ti6Al4V and AA6061-T6 appear to be particularly active in terms of  $N_2O_4$  decomposition, while 304LSS and Inconel X750 affect  $N_2O_4$  decomposition at almost the same rates experienced in  $N_2H_4$  and MMH for short term tests.

Where possible, the results of these tests were compared to existing real-time data reported by other investigations (Refs. 7-10). However, in most cases the previously published results are semi-quantitative at best. For example, it has been reported in Ref. 7 that Ti6Al4V and 304LSS are virtually

TABLE VII

Exchange Current Densities  
For  $N_2H_4$ , MMH and  $N_2O_4$

(Two Days Exposure)

Metal	$i_0$ ( $\mu a/cm^2$ )		
	* $N_2H_4$	*MMH	** $N_2O_4$ (15% $H_2O$ )
AA6061-T6	$3.00 \times 10^{-2}$	$6.7 \times 10^{-3}$	$1.50 \times 10^{-1}$
Ti6Al4V	$2.12 \times 10^{-2}$	$1.27 \times 10^{-2}$	$6.70 \times 10^{-1}$
304L SS	$2.08 \times 10^{-1}$	$3.18 \times 10^{-2}$	$5.64 \times 10^{-2}$
Inconel X 750	$2.80 \times 10^{-1}$	$4.0 \times 10^{-2}$	$6.10 \times 10^{-2}$
Pt-10% Ir	$2.02 \times 10^{-3}$	$5.4 \times 10^{-2}$	$3.31 \times 10^{-1}$

\*  $N_2H_4$  and MMH at 110 F

\*\*  $N_2O_4$  at 50 F

TABLE VIII

Decomposition Rates For  
 $N_2H_4$ , MMH and  $N_2O_4$

(Two Days Exposure)

Metal	(mg/cm <sup>2</sup> /yr)		
	* $N_2H_4$	*MMH	** $N_2O_4$ (15% $H_2O$ )
AA6061-T6	0.008	0.051	2.248
Ti6Al4V	0.055	0.096	10.04
304L SS	0.542	0.239	0.845
Inconel X 750	0.730	0.301	0.914
Pt-10% Ir	0.526	0.406	4.960

\*  $N_2H_4$  and MMH at 110 F

\*\*  $N_2O_4$  at 50 F

unattacked by  $N_2O_4$  containing up to 3.2 percent  $H_2O$  at temperatures up to 165 F. However, Rocketdyne (Ref. 11) and AFRPL (Ref. 12) report that titanium is not satisfactory for use with  $N_2O_4$ . Titanium compatibility problems appear to be due to the presence of oxygen, and can be corrected by the addition of small amounts of NO to reduce the oxygen level. This approach has also been applied to Inconel. In general, it is concluded in Ref. 7 that AA6061-T6 and the three-hundred-series stainless steels are compatible materials.

Hercules (Ref. 8) rates the  $N_2O_4$  compatibility of AA6061-T6 and 304SS as excellent (penetrations of <1 mil/yr) at temperatures up to 140 F and water concentration levels on the order of 0.1 percent. Salvinski, et al., (Ref. 9) studied the compatibility of  $N_2O_4$  with a wide variety of materials, including AA6061-T6 and Ti6Al4V, and reported the results in terms of impurities which were deliberately added to the system. The test temperature was 165 F and the test durations were one and four months. Approximately 0.9 weight percent water was added. Upon removal of the test specimens, the AA6061-T6 samples were found to be covered with a thick white coating. This result was accompanied by a reduction in the water content of the  $N_2O_4$ . However, the Ti6Al4V sample was virtually unaffected under the same conditions. No quantitative data was reported.

Toth, et al., (Ref. 10) studied AA6061-T6 and Ti6Al4V in  $N_2O_4$  for real time periods up to approximately four years. Post test analysis indicated no evidence of appreciable oxidizer decomposition for either metal. The water content was not measured but was estimated to be approximately 0.02 to 0.05 weight percent. There was 50 ppm Al present in the  $N_2O_4$  solution which had been exposed to AA6061-T6. In addition, the specimen was covered with a uniform white tarnish. The Ti6Al4V specimen emerged with a spotty gray corrosion film; however, no residue was found and the  $N_2O_4$  solution contained 2 ppm Al, 1 ppm V and less than 2 ppm Ti. It is apparent that at low water concentrations (less than 0.05 percent) there is no appreciable  $N_2O_4$  induced corrosion of the metals studied. There was a slight (0.1 percent) weight gain for Ti6Al4V and a .007 percent weight loss for AA6061-T6 (Ref. 10). There was no evidence of any  $N_2O_4$  decomposition.

#### DISCUSSION AND CONCLUSIONS

The results of the nitrogen tetroxide feasibility study suggest that at very low water concentrations (less than one percent)  $N_2O_4$  does not react on metal surfaces in any measurable amounts. Even when water is deliberately added to the system, it is necessary to achieve water contents equivalent to



High Density Acid (HDA) type systems ( $\text{N}_2\text{O}_4\text{-HNO}_3$ ) in order to achieve measurable decomposition rates. Neither the single-phase region, below about two percent water concentration, nor the two-phase region, up to about 10 percent water concentration, was sufficiently conductive for electrochemical measurements, even in systems where the electrode spacing was on the order of 2 to 4 mm.

Comparison of the data obtained in this study, with information available in the literature, indicates that the lack of any appreciable metal attack in the presence of propellant grade  $\text{N}_2\text{O}_4$  is typical of  $\text{N}_2\text{O}_4$ -metal systems with a low water content.

Thus real-time results coupled with the results of the present feasibility study indicate that drastic contamination of  $\text{N}_2\text{O}_4$  is necessary before any appreciable corrosion and/or propellant decomposition takes place. In the present study none of the test pieces were corroded or even tarnished by the contaminated  $\text{N}_2\text{O}_4$ . However, it should be noted that as soon as the water content of  $\text{N}_2\text{O}_4$  is sufficiently high to cause the formation of two phases, the acid rich phase will result in HDA type nitric acid corrosion in localized zones (i.e., crevices, etc.). Electrochemical measurements were made in this region and relatively high decomposition rates were noted.

It is suggested that future investigations of  $\text{N}_2\text{O}_4$ -material compatibility emphasize detailed studies of the high-acid side of the two-phase region. These studies should include consideration of the localization of the high density phase at crevice positions, such as valve seats and swage type fittings.

#### REFERENCES

1. Brown, C. T.: Determination of Long-Term Compatibility of Hydrazine with Selected Materials of Construction. Final Report, AFRPL-TR-76-21, United Technologies Research Center, East Hartford, Connecticut, May 1976.
2. Brown, C. T.: Determination of Long-Term Compatibility of Hydrazine with Selected Materials of Construction. Design Criteria and Guidance, AFRPL-TR-76-33, June 1976.
3. Mansfeld, F.: The Polarization Resistance Technique for Measuring Corrosion Currents. Advances in Corrosion Science and Technology, Rockwell International Science Center, Thousand Oaks, California.

REFERENCES (cont'd)

4. Brown, C. T.: Demonstration of Feasibility of the Electrochemical Method for Monomethylhydrazine Compatibility Testing. UTRC Report R77-912837-10, December 1977.
5. Bradley, R. S.: The Electrical Conductivity of Solid and Liquid Nitrogen Dioxide. Trans. Faraday Soc. 52 1255-9 (1956).
6. Angus, W. R., R. W. Jones and G. O. Phillips.: Existence of Nitrosyl Ions in Nitrogen Tetroxide. Nature 164, p. 433 (1949).
7. Bell Aerosystems Company, Propellant Properties Manual, Vol. I, Oxidizers.
8. Hercules, Inc., Nitrogen Tetroxide, Section 3, Handling and Storage (1968).
9. Salvinski, R. J., et al.: Advanced Valve Technology, Vol II, Materials Compatibility and Liquid Propellant Study, TRW Report, November 1967.
10. Toth, L. R., et al.: Propellant/Material Compatibility Program and Results. NASA Technical Memorandum 33-779, August 1976.
11. Rocketdyne Division of North American Aviation, Nitrogen Tetroxide Handling Manual. Report No. AF/SSD-TR-61-8 (Rocketdyne Report R-3135), September 1961.
12. Rocket Propulsion Laboratory, Handling and Storage of Nitrogen Tetroxide. Report No. RTD-TDR-63-1033, Edwards AFB, California, May 1963.